

UV-ACTIVATED CHLORINATION PROCESS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of international patent application no.

- 10 PCT/DE00/01953, filed June 14, 2000 designating the United States of America, the entire disclosure of which is incorporated herein by reference. Priority is claimed based on Federal Republic of Germany patent application no. DE 199 27 394.4, filed June 16, 1999.

15 BACKGROUND OF THE INVENTION

The invention relates to a process for producing certain chlorine-containing alkanes through UV-light supported chlorination.

- It has long been known that elemental chlorine under incident light radiation will attach to unsaturated carbon compounds or that an exchange of hydrogen for
20 chlorine will occur.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a new process for producing chlorine-containing alkanes.

- 25 Another object of the invention is to provide a process for producing chlorine-containing alkanes with a high reaction rate and high selectivity.

These and other objects are achieved in accordance with the present invention as described and claimed hereinafter.

- The process according to the invention for producing chlorine-containing
30 alkanes selected from the group consisting of pentachloroethane, 1,1,1-trifluoro-2,2,2-trichloroethane, 1,1,1-trifluoro-2,2-dichloroethane and 1,1,1,2-tetrachloro-2,2-difluoroethane by attaching chlorine to starting compounds with C-C double bonds or by exchanging hydrogen for chlorine, and for producing purified 1,1,1,3,3-

pentafluorobutane from 1,1,1,3,3-pentafluorobutane that has been contaminated with compounds with C-C double bonds or C-C triple bonds by chlorinating these unsaturated compounds, provides that the starting compound in the gas or the liquid phase is brought into contact with elemental chlorine and is irradiated with UV light
5 with a wavelength of $\lambda \geq 280$ nm.

It is possible to work in the liquid phase or in the gas phase. Generally, one can work at a temperature ranging from room temperature to 200°C and at a pressure of 1 to 10 bar (absolute). The reaction temperature and the pressure are selected in such a way that the starting compound to be treated, or the starting mixture, is present in the gas
10 phase or the liquid phase. One variant of the invention concerns its use as a production process. Another variant concerns its use as a purification process. The use as a production process will first be described in greater detail.

Particularly preferably, the process is used to produce pentachloroethane from trichloroethylene, to produce 1,1,1,2-tetrachloro-2,2-difluoroethane from 1-chloro-1,1,1-
15 difluoroethane, and to produce 1,1,1-trifluoro-2,2,2-trichloroethane from 1,1,1-trifluoro-2,2-dichloroethane.

The molar ratio of starting compound to elemental chlorine ranges from 1 : 0.1 to 1 : 10 when attaching chlorine and from 1 : 0.01 to 1 : 5 when exchanging hydrogen for chlorine. If only one of two H atoms is to be exchanged in the exchange of hydrogen
20 for chlorine, the ratio of starting compounds to chlorine falls in the upper range (lower chlorine content). Preferably, the chlorine is used in an amount that is 0.9 times to 1.3 times the stoichiometrically required amount.

Another variant of the invention concerns the purification of 1,1,1,3,3-pentafluorobutane (HFC-365mfc) with the aim of separating photochlorinatable olefinic
25 impurities. It has been shown that the olefinic impurities, which are production-related, can essentially be selectively converted by the inventive photochlorination and separated in a simplified manner in the form of chlorination products.

For irradiation, it is advantageous to use radiation lamps (e.g., Philips fluorescent tubes) that only emit (UV) light of a wavelength at or above 280 nm ($\lambda \geq$
30 280 nm). In such case, it is possible to irradiate through quartz glass. The only prerequisite for this variant is that these lamps emit in the absorption range of the elemental chlorine. Alternatively, it is possible to use radiation lamps (e.g., Hg medium or high-pressure discharge lamps), which also emit some lines in the range below 280

nm ($\lambda < 280$ nm). In this variant, irradiation has to occur through a glass that is transparent only for light with a wavelength of 280 nm or above ($\lambda > 280$ nm), i.e., that filters out the shorter wave radiation component of $\lambda < 280$ nm. Well suited are, for instance, borosilicate glasses. This type of glass typically contains 7 to 13% B_2O_3 , 70 to 80% SiO_2 , furthermore 2 to 7% Al_2O_3 and 4 to 8% $Na_2O + K_2O$ and 0 to 5% alkaline-earth metal oxides. Known trademarks for borosilicate glasses are Duran, Pyrex and Solidex. It is of course also possible to proceed by using on the one hand a radiation lamp that emits light above the indicated wavelengths and, in addition, glasses that are transparent for light above the indicated wavelength (i.e., that are non-transparent for light below the indicated wavelength).

Also suitable for irradiation are lamps, e.g., Hg high-pressure discharge lamps, which due to a dopant emit primarily, or only, in the wavelength range at or above 280 nm. Hg high-pressure discharge lamps, for instance, have a rather intensive band in the range of 254 nm which is filtered out, e.g., by borosilicate glass, as described above. In Hg high-pressure discharge lamps that are doped with metal iodides, this line is strongly suppressed. Surprising in these doped lamps is the frequently more than proportional increase in the conversion rate. Excellent results with respect to conversion rate and selectivity are obtained with Hg high-pressure discharge lamps that are doped with gallium iodide and especially with lamps that are doped with thallium iodide or cadmium iodide. Even with the use of this type of lamp, it is preferable to use glass that filters out the shorter wave radiation component of $\lambda \leq 280$ nm. It is suitable and technically advantageous to use the entire radiation range with wavelengths above and below said limits.

HFC-365mfc can be purified in the liquid phase or in the gas phase. Pentachloroethane is advantageously produced in the liquid phase. CFC-112a, CFC-113a and HCFC-123 are advantageously produced in the gas phase. Continuous operation is especially facilitated by working in the gas phase.

In the gas phase, the process is advantageously conducted in a flow-through apparatus. The starting material (the corresponding hydrogen and halogen-containing starting compounds and chlorine) is continuously fed into the flow-through apparatus and the reaction product is continuously withdrawn in proportion to the amount introduced.

The average residence time in the reaction vessel is preferably between 0.01 and 30 minutes, preferably between 0.01 and 3 minutes, particularly preferably between 0.5 and 3.0 minutes. Good results can be achieved even if the residence times are very short, e.g., between 0.04 and 0.5 minutes. The optimum average residence time, which
5 depends, among other things, on the lamp output and on the geometric parameters of the radiation apparatus (flow-through apparatus) can be determined by simple manual tests and analysis of the product stream, e.g., by gas chromatography.

Better conversion rates and higher selectivity can be achieved by using, instead of a single radiation lamp with a certain output, two or more lower-output lamps with
10 an equivalent total output in reactors that are connected in series. The product is then advantageously separated after leaving the corresponding reactions, e.g., by freezing it out. Proper swirling of the reaction mixture, e.g., by suitable installations in the reactor, is also often advantageous. In the liquid phase, it is preferred to work in batches. The process has the advantages of high conversion at high selectivity.

15 The following examples are intended to illustrate the invention in greater detail without limiting its scope.

Examples 1 to 6:

Production of 1,1,1-trifluoro-2,2,2-trichloroethane (CFC-113a) through
20 photochlorination of 1,1,1-trifluoro-2,2-dichloroethane (HCPC-123) through Duran 50 with light with a wavelength of $\lambda > 280$ nm.

Apparatus: double shell glass reactor (double shell for oil heating) with a submersible shaft made of *Duran*® 50 (400 ml reaction volume), equipped with a submersible Hg discharge lamp TQ 718 by Heraeus-Noblelight with water cooling. The 1,1,1-trifluoro-
25 2,2-dichloroethane was evaporated with a pre-evaporator and was introduced from below as a gas into the reactor together with the chlorine (mixed). The product stream exited at the top. The reaction temperature was 110°C. The gas stream exiting the reactor was analyzed by gas chromatography (GC) (sampling in the gas collection tube).

Tests 1 to 6 conducted with different chlorine feeds:

| Test | mole % Chlorine | Conversion Rate | 113a Selectivity |
|------|-----------------|-----------------|------------------|
| 1 | 10 | 3.79 | 99.13 |
| 2 | 30 | 5.18 | 99.04 |
| 3 | 60 | 17.41 | 97.7 |
| 4 | 90 | 31.94 | 98.29 |
| 5 | 120 | 80.63 | 95.9 |
| 6 | 150 | 100 | 97.3 |

* Analysis data provided in GC surface percent

Examples 7 to 11 (Comparison Tests):

- 5 Production of 113a by photochlorination of 123 through quartz glass

Apparatus: double shell glass reactor (double shell for oil heating) with submersible shaft made of *quartz glass* (400 ml reaction volume) equipped with submersible Hg discharge lamp TQ 718 of Heraeus Noblelight with water cooling. The 1,1,1-trifluoro-2,2-dichloroethane was evaporated and introduced from below as a gas into the reactor together with the chlorine. The product stream exited at the top. The reaction temperature was 110°C.

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Tests 1 to 5 conducted with different chlorine feeds:

| Test | mole % Chlorine | Conversion Rate | 113a Selectivity |
|------|-----------------|-----------------|------------------|
| 7 | 10 | 1.44 | 96.4 |
| 8 | 30 | 13.5 | 95.64 |
| 9 | 60 | 13.4 | 90.1 |
| 10 | 90 | 26.64 | 93.5 |
| 11 | 120 | 77.24 | 79.17 |

* Analysis data provided in GC surface percent

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Example 12:

Removal of olefinic byproducts from 1,1,1,3,3-pentafluorobutane (365mfc) through photochlorination with $\lambda > 280$ nm

a) Laboratory Tests

- 20 50 g samples of 365mfc contaminated with 7,000 ppm $C_4ClF_3H_4$ (two isomers) were disposed, respectively, in two 100-ml Duran® 50 glass flasks and agitated.

Thermal Test:

Immediately after adding 0.4 g (5.6 mmole) chlorine, the one flask was wrapped in aluminum foil. After 24 h the sample was examined by gas chromatography. Out of the 7,000 ppm $C_4ClF_3H_4$ (2 isomers), 4,450 ppm were still detected, but the 365mfc content was reduced by well over 1%.

Photochemical Test:

The second flask, after adding 0.2 g (2.8 mmole) chlorine, was irradiated overnight with a Philips fluorescent lamp (Philips reflector lamp No. 1099415, 40 W output).

Subsequently, the sample was examined by gas chromatography. Out of the 7,000 ppm $C_4ClF_3H_4$ (2 isomers), 160 ppm were still detected, but the 365mfc content was almost unchanged. A further addition of 0.2 g (2.8 mmole) chlorine and irradiation overnight resulted in an amount of $C_4ClF_3H_4$ that was no longer detectable (<0.1 ppm, SIM run, GS-MSD), again with a nearly constant 365mfc content.

b) Technical Test

Test setup: Pfaudler reactor ($V = 100$ l) with mounted glass column with top cooler (water cooling). In the cover of the Pfaudler reactor, a submersible Hg discharge lamp TQ 718 by Heraeus Noblelight was installed with a submersible tube made of Duran 50 glass. Irradiation thus took place at a wavelength of $\lambda > 280$ nm. The output was adjusted to 700 W.

Procedure: The 365mfc was pumped into the Pfaudler reactor. One half hour prior to chlorine metering, the submersible Hg discharge lamp (700 watt) was turned on while mixing. Through a submersible tube, approximately 20 l/h of chlorine were added until no olefins could be detected in the SIM run of the GC-MSD. After chlorination was completed, the submersible Hg discharge lamp was operated for another hour. The 365mfc thus treated was discharged and precision distilled in a distillation column (height: 3 m, diameter 100 mm, filled with 10 mm Raschig glass packing).

Test 12.1: 62.3 kg educt treated with 40.9 g chlorine / test duration 3 hours.
GC analysis of educt (before photochlorination): 99.5 w/w % 365mfc,
Total $C_4ClF_3H_4$: 0.112 w/w %

GC analysis of product (after photochlorination): 99.4 w/w % 365mfc,
 Total $C_4ClF_3H_4$: < 10 ppm

Test 12.2: 62.0 kg educt treated with 110.9 g chlorine / test duration 5 hours.

Analysis of educt: 99.7% 365mfc,

5 Total $C_4ClF_3H_4$: 0.210%

Analysis of product: 99.6 w/w % 365mfc,
 Total $C_4ClF_3H_4$: < 10 ppm

Purification: The fractions obtained from the tests were combined and precision
 distilled in the glass column. Their purity after distillation was 99.98%
 10 w/w % 365mfc.

Example 13:

Production of pentachloroethane (120) from trichloroethylene through
 photochlorination with $\lambda > 280$ nm

15 a) Photochlorination test on a 5 l scale

Test setup: A 5 liter double shell vessel of Duran 50 glass with mounted reflux
 condenser, bubble counter and submersible tube with diffuser. The
 vessel also contained a water-cooled cooling coil. The vessel was
 irradiated from the outside with a Philips fluorescent tube (Philips
 20 reflector lamp No. 1099415, 40 Watts output).

Procedure: 3.24 kg (24.7 moles) trichloroethylene were filled into the vessel and
 heated to 60°C (thermostat, connected to double shell). Subsequently,
 1.926 kg (27.17 moles) chlorine was metered such that no chlorine was
 penetrating through or exiting the apparatus through the bubble counter.
 25 The reaction was completed after 3 hours.

Purification: The resulting pentachloroethane had a 99.4% degree of purity (rest:
 unconverted trichloroethylene and hexachloroethane) and can be used
 without further purification.

b) Technical Photochlorination Test

30 Test setup: Pfaudler reactor ($V = 100$ l) with mounted glass column with top cooler
 (water cooling). In the cover of the Pfaudler reactor, a submersible Hg
 discharge lamp TQ 718 by Heraeus Noblelight was installed with a

submersible tube made of Duran® 50 glass. Irradiation thus took place at a wavelength of $\lambda > 280$ nm. The output was adjusted to 500 Watts.

Procedure: 65.7 kg (507 mole) trichloroethylene was filled into the Pfaudler reactor and heated to 60°C and mixed. Subsequently, after lighting and burning in the lamp, 35.36 kg (500.1 mole) chlorine was introduced such that the chlorine did not penetrate through.

Purification: At the end of the test, without any further purification, the pentachloroethane produced had a degree of purity of 99.1% (GC %); remainder: trichloroethylene and hexachloroethane.

Example 14 (Comparison Example):

Thermal Chlorination

14a) Thermal chlorination of Trichloroethylene

50 g (0.381 mole) trichloroethylene was combined with 28 g (0.423 mole) chlorine in a 250 ml Roth autoclave and placed into an oil bath preheated to 100°C. When an internal temperature of about 50°C was reached, marked exothermia developed and the autoclave content was discharged through the bursting disk into the outlet.

14b) Thermal Test on a 5 liter Scale

Test setup: A 5 liter double shell vessel of Duran 50 glass with mounted reflux condenser, bubble counter and submersible tube with diffuser. The vessel also contained a water-cooled cooling coil. The apparatus was completely covered with aluminum foil.

Procedure: 3.24 kg (24.7 mole) trichloroethylene was introduced into the vessel and heated to 60°C (thermostat, connected to double shell). Subsequently, 1.926 kg (27.17 mole) chlorine was metered such that no chlorine was penetrating through or exiting the apparatus via the bubble counter. After 15 hours, the introduction of chlorine was completed.

Purification: The resulting pentachloroethane had a purity of 83.3% (residue: unconverted trichloroethylene and large amounts of hexachloroethane).

Examples 15 to 19:

Production of 1,1,1-trifluoro-2,2-dichloroethane (123) from 1,1,1-trifluoro-2-chloroethane (133a) through photochlorination with $\lambda > 280$ nm.

5 General setup and execution for tests 15 to 19:

A mixture of 94.8 g (0.80 mole) 133a and a variable amount of chlorine were mixed and introduced in the form of a gas into a photochemical reactor holding 4.3 liters (diameter 100 mm, wall thickness 2 mm) made of Duran® 50. The reaction temperature during the 30-minute tests was 40°C. Irradiation was effected by 3 x 40 W UV lamps from Philips, type "Cleo Performance R-UVA 40 Watts" The lamps were cylindrically arranged around the photochemical reactor. The tests were evaluated by GC analysis of the reactor exhaust gas.

Example 15:

15 Feed: 94.8 g (0.80 mole) 133a, 5.67 g (0.08 mole) chlorine
Result: Conversion: 13.98%
 Selectivity 123: 86%
 Selectivity 113a: 13%

20 Example 16:

Feed: 94.8 (0.80 mole) 133a, 17.01 g (0.24 mole) chlorine
Result: Conversion: 25.2%
 Selectivity 123: 74%
 Selectivity 113a: 26%

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Example 17:

Feed: 94.8 (0.80 mole) 133a, 34.03 g (0.48 mole) chlorine
Result: Conversion: 38.8%
 Selectivity 123: 57.4%
30 Selectivity 113a: 42%

Example 18:

Feed: 94.8 (0.80 mole) 133a, 51.05 g (0.08 mole) chlorine

Result: Conversion: 45.8%
Selectivity 123: 47%
Selectivity 113a: 53%

5 Example 19:

Feed: 94.8 (0.80 mole) 133a, 68.06 g (0.96 mole) chlorine
Result: Conversion: 51%
Selectivity 123: 44.3%
Selectivity 113a: 56%

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Example 20:

Photochlorination of 142b to produce 112a

The reaction was performed analogously to Examples 1 to 6. Conversion and yield were comparable to the results from the production of 113a.

15 The foregoing description and examples have been set forth merely to illustrate the invention and are not intended to be limiting. Since modifications of the described embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed broadly to include all variations falling within the scope of the appended claims and equivalents thereof.